Patents

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
Ow et al.	)	
Serial No.: **09/121,152**	)	Art Unit: **1731**
Filed: **May 6, 1994**	)	Examiner: **Steve Alvo**
For: **BIOLOGICAL DE-INKING METHOD**	)	

DECLARATION OF KARL-ERIK L. ERIKSSON, PH.D. UNDER 37 CFR § 1.132

KARL-ERIK L. ERIKSSON, PH.D., declares as follows:

1. I earned a Dr. Sci. in biochemistry in 1967. Subsequently, I have conducted extensive research in the fields of enzymology, microbiology and biochemistry at the Swedish Forest Products Research Laboratory and as a Professor of Biochemistry and Eminent Scholar at the University of Georgia, Athens, Georgia. I currently am working in Sweden and am involved with several organizations involved with the commercialization of biological-based innovations in the pulp and paper industry. Attached is a copy of my Curriculum Vitae.

2. My declaration is based on my scientific experience and understanding of the subject matter as an expert in the art. I am familiar with the invention described in the above-identified patent application regarding the novel use of deinking enzymes under non-alkaline conditions. For the record, I have a small economic interest in the business concern that has licensed the subject invention .

3. I have read the English translation of Japanese Patent 59-9299 ('299 patent). In my expert opinion, the '299 patent, read in its entirety, teaches one of ordinary skill in the art only the successful use of deinking enzymes with alkaline deinking chemicals. It is my opinion that the data provided in the '299 patent, taken together with the knowledge of one skilled in the art prior to the priority date of the present application of May 16, 1989, does not provide an expectation for the successful use of enzymes for removing ink from pulp in a non-alkali

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K-E Eriksson Pulp & Paper Biotechnology Handelsbolag
Rödbosundsvägen 17
184 60 Åkersberga
Tel: +46 8 540 639 59
E-mail: k-erik.eriksson@telia.com
Bankgiro 5535-6020
SEB 5366-10 016 98

DECLARATION OF KARL-ERIK L. ERIKSSON, PH.D.

environment, in particular at a pH of between about 3 to about 8.

4. This is true because the overall thrust of the '299 patent specification, and the evidence provided in all preferred embodiments and in all the Examples, refer to only alkaline deinking conditions. The statement on page 2, last full paragraph, to page 3, end of carryover paragraph, that

> [a]ccordingly, this invention provides a de-inking agent for recycling old paper, containing cellulase. Cellulase commonly occurring in plants, animals, bacteria and fungi can be used in this invention without any special restriction, but alkaline cellulase is especially preferred. Alkaline cellulase is one having optimum pH 8.0 – 11.5 (preferably 8.1 - 11.0). Such enzyme retains its activity in the alkaline range as well as the acid or neutral range, e.g. a product purified and fractionated from cellulase culture liquid of various origins by salting out, precipitation, dialysis and gel fractionation . . .

refers to the conditions under which the enzyme may be purified, and does not suggest the use of the enzyme for deinking under non-alkaline conditions. Even if one were to interpret the statement to indicate the use of the enzyme under non-alkaline conditions, one skilled in the art would not have expected a successful result deinking under non-alkaline conditions, for the reasons described below. The only scientifically supported statements in the '299 patent are directed to the use of deinking enzymes in alkali conditions.

5. A possible reading of the '299 patent is that it is possible for cellulase enzymes to have activity at all pH ranges, but one skilled in the art at the time of this invention would not have tried to <u>deink</u> at a neutral pH, or non-alkaline conditions, because it was thought that alkaline conditions were required to achieve the swelling of the fibers necessary to remove the ink particles.

6. Before the description in the above-identified patent application, it was believed that alkaline conditions were necessary to cause ink containing paper fibers to swell to effect defiberization and deinking by enzymes. Absent alkaline conditions, one would not have expected swelling, and therefore deinking, to occur as a result of the addition of deinking enzymes alone in the pulping process. In the deinking art there is over twenty years of published detailed studies from commercial, academic and government laboratories that emphasize that chemical modification and treatment by alkali exposure is essential and necessary for deinking. As a recent example, enclosed is a copy of the Paper and Pulp

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International (PPI) publication entitled "Neutral Deinking Makes Its Debut," describing the breakthrough in October 1993 of deinking in neutral conditions, without the addition of alkalis such as sodium hydroxide to the pulp prior to or during deinking.

7. Therefore, to one skilled in the deinking art at the time the above-identified application was originally filed, the deinking action of enzymes in a non-alkaline medium would have been both novel and surprising. An expectation of the successful use of deinking enzymes in an aqueous medium having a pH of between about 3 to about 8 is not found in the '299 patent. It is my opinion that prior to the invention described in the above-identified patent application, no one skilled in the art would have considered evaluating deinking enzymes alone without the addition of alkalis.

8. In summary, it is my expert opinion that the disclosure of the '299 patent supports only the deinking of waste papers by the use of chemical alkaline deinking agents and cellulase, and does not provide a basis for the successful use of cellulase deinking enzyme in an aqueous medium having a pH of between about 3 to about 8 with an expectation of successful deinking of waste paper.

9. The undersigned declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment or both under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

March 19, 2004
DATE

Karl-Erik Eriksson
KARL-ERIK L. ERIKSSON, PH.D.

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DECLARATION OF HARALD SCHMID UNDER 37 CFR § 1.132

HARALD SCHMID, declares as follows:

1. I earned an Engineer Diploma in 1992 from Munich University. My principal course of study was in Pulp and Paper Science. Subsequently, I have worked in the pulp and paper industry my entire career in Germany, Switzerland, and the United Kingdom. I am an expert in deinking chemistries in which I worked almost exclusively during, and shortly after, my time at Munich University.

2. My declaration is based on my scientific experience and understanding of the subject matter as an expert in the art. I am familiar with the invention described in the above-identified patent application regarding the novel use of deinking enzymes under non-alkali conditions.

3. I have reviewed the article contained in the Paper and Pulp International (PPI) publication entitled "Neutral Deinking Makes Its Debut," describing the breakthrough in October 1993 of deinking in neutral conditions, without the addition of alkalis such as sodium hydroxide to the pulp prior to or during deinking.

4. That publication refers to the use of deinking at neutral conditions at the Zwingen mill in Switzerland.

5. That mill is owned by Zwingen AG and is based in Zwingen, Switzerland. I was project manager at the Zwingen mill. I was directly involved with the design, construction, and early operation of their new deinking plant which began operation in

DECLARATION OF HARALD SCHMID

May 1993.

6. The Zwingen mill deinks a variety of wastepaper grades using the floatation process. The Zwingen mill produces an assortment of paper grades including book paper, business form paper and photocopy based paper.

7. In 1992, I worked with the Zwingen mill owners to design the mill around a neutral deinking concept. It is my understanding and belief as one of skill and knowledge in the art at that time that the Zwingen mill was the first of its type in the world intended to be built and run on a neutral flotation deinking concep. There was no suggestion of non-alkali deinking at the Zwingen plant of which I was aware prior to 1992. The concept was tested and proven as effective in a pilot plant trial in 1992. The pilot plant trial created the proof to proceed with the design and the construction of the deinking plant in 1992, which concluded with the start up of the deinking plant in May of 1993.

8. The undersigned declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements are made under 18 U.S.C. § 1001 and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

7.5.2004
DATE

HARALD SCHMID

Suppliers of deinking systems are working to meet the demand for high-quality paper made from low-quality waste. Amanda Marcus rounds up the latest developments and lists new orders worldwide.

ATTACHMENT 1

Neutral deinking makes its debut

SOME RECENT AND PLANNED DEINKING INSTALLATIONS[1]

Country	Company	Mill location	Startup date	Capacity (1,000 tons/yr)	Wastepaper	Grade	End-use Supplier
Australia	Australian Newsprint Mills	Lavington, NSW	1993	122.5*	News/magazines	Newsprint	Voith
Austria	Leykam-Mürztaler	Gratkorn	1993	40*	News/magazines	Newsprint	Voith[2]
Argentina	Celulosa Campana	Zarate	1994	45.5	Mixed waste	Tissue	Sulzer Papertec
Argentina	Papel Prensa	Buenos Aires	1993	21	Waste	Newsprint	Lamort
Canada	Alberta Newsprint	Whitecourt	1993	21*	News/magazines	Newsprint	Voith[3]
Canada	QUNO (Quebec & Ontario Pap)	Thorold	1993	70*	News/magazines	Newsprint	Voith[3]
Canada	Spruce Falls Power & Paper	Kapuskasing	1993	87.5*	Old news/pamphlets	Newsprint	Voith[3]
China	Guangzhou Paper	Guangzhou	1993	32	Ledgers	Fine paper	Black Clawson
China	Hanzhong Pulp & Paper	-	1994	9	Waste	Whiteboard base	Lamort/Aikawa
China	Xuecheng Huazhong Paper	-	1993	9	Waste	Whiteboard base	Lamort/Aikawa
China	Yanjin Paper	Nanping	1994	35*	News/magazines	Newsprint	Beloit
France	Chapelle Darblay	Pont Audemer	1993	6	Ledgers	Fine paper	Black Clawson
Germany	Dresden Papier	Freital	1994	42	News/magazines	Graphic papers	Sulzer Papertec
Germany	Palm	Eltmann	1994	168	News/magazines	Newsprint	Sulzer Papertec
Germany	Sachsen Papier	Eilenburg	1994	350	News/magazines	Newsprint	Sulzer Papertec
Germany	Schwedt Pap. und Karton	Schwedt	1994	143.5	News/magazines	Graphic papers	Sulzer Papertec

*1: This list is not intended to be comprehensive. Orders since the last PPI Deinking Survey in October 1992. 2: Built by Voith St. Pölten, Austria, a Voith licensee. 3: Built by Voith Appleton, USA, a Voith licensee. 4: Andritz was acting as a licensee of Sulzer Papertec, Germany. * = Calculated from daily capacity, on the basis of 350 production days/yr.*

Continued on page 24

WASTE IS NO LONGER a dirty word. On the contrary, an increasing number of consumers, and hence papermakers, can't seem to get enough of it. According to PPI statistics (see table), the world recovered almost 92 million tons of wastepaper in 1992, up from 87 million tons in 1991, and consumed 95.5 million tons, four million tons more than the previous year. The world's average utilization rate has risen by two points to 39%.

From Argentina to Austria, and Mexico to Morocco, the latest reference lists from suppliers *(see above)* show that mills are still spending money on waste treatment systems, even during a time of severe cutbacks in capital investment in the industry. Increasing environmental legislation and stringent quality requirements are demanding rapid developments from manufacturers of deinking equipment. This article rounds up the latest news from some of the sector's major suppliers.

All agree that differences in customer demands in Europe and North America are narrowing. Black Clawson, USA, reports that US customers are beginning to look at the European approach to projects, looking for more liability from the supplier to make the system perform. "As more of these projects come under study, it is becoming apparent that the vendor's ability to provide special financing or equity participation is becoming as important as the technological issues that have always faced us," comments Black Clawson.

The parameters of evaluation from the customers' viewpoint are basically the same: All mills are seeking price performance, higher brightness, dirt reduction, ash control and higher yields from their systems: no mean task for suppliers.

Customers want more for less

One of the major challenges facing suppliers of wastepaper treatment systems is that mills are using lower-quality and hard-to-deink waste while requiring ever-higher quality. As a result, according to Black Clawson, research in the USA is focusing largely on the removal of diffic- handle debris that is typically grade office papers: unbleached fibers, laser-printing inks, UV coatings and some dyed papers. The supplier adds that it is only a matter of time before the same concerns are transferred to system designers in the European and Asian markets.

Mills get into neutral gear

Neutral deinking is being hailed as the latest breakthrough in waste treatment technology by Lamort of France. It says that the benefits of deinking in neutral media are proving to be far beyond initial expectations. Such a solution is attractive because it requires less chemicals, so chemical oxygen demand is reduced and companies save on chemical costs. Suppliers to the industry say that controllability, drainage, pulp strength, bleachability and screening efficiency are all better than with conventional deinking techniques.

The Stephenson Group, UK, which supplies deinking chemicals, agrees that demand for neutral deinking solutions and closed-water circuits is growing: Custom- want to use lower and lower grades of

wastepaper for deinking, comments the company, and this is leading to problems with product quality (both brightness and stickies), which the customer expects the supplier to solve.

In response, a considerable amount of resources is being invested in upgrading washing systems as part of a "complete ink removal" solution provided by a combined wash/flotation system. Cost is the limiting factor, explains Stephenson, but work on the concept is continuing.

The first neutral deinking system using household waste to make graphic papers is already in operation at Zwingen in Switzerland. The line started up last July and is the result of a joint project between the mill, French supplier Lamort, and Dr. W. Kolb. Lamort explains that since the process does not use sodium hydroxide, an efficient fiber-to-fiber friction is imperative if good ink removal is to be achieved at the pulping stage, although post-flotation is still available. Lamort recommends its Helico pulper for such applications.

Waste is floating on air

Neutral flotation is quite different to conventional deinking in that the ink particles adhere directly to the air bubbles, Lamort explains. The foam structure of the cell is also completely different. Consequently, demand is growing for a flotation cell which can handle an increased number of smaller bubbles and separate foam from fiber. Lamort's response is the Verticel which works on the concept of injection and has a controlled flow pattern.

Lamort says that Verticel has a foam-removal system which is particularly suited to neutral deinking.

Voith, Germany, is also continuing work on flotation and has recently launched its new laboratory flotation cell type E, a reduced version of the industrial unit. Five have already been sold.

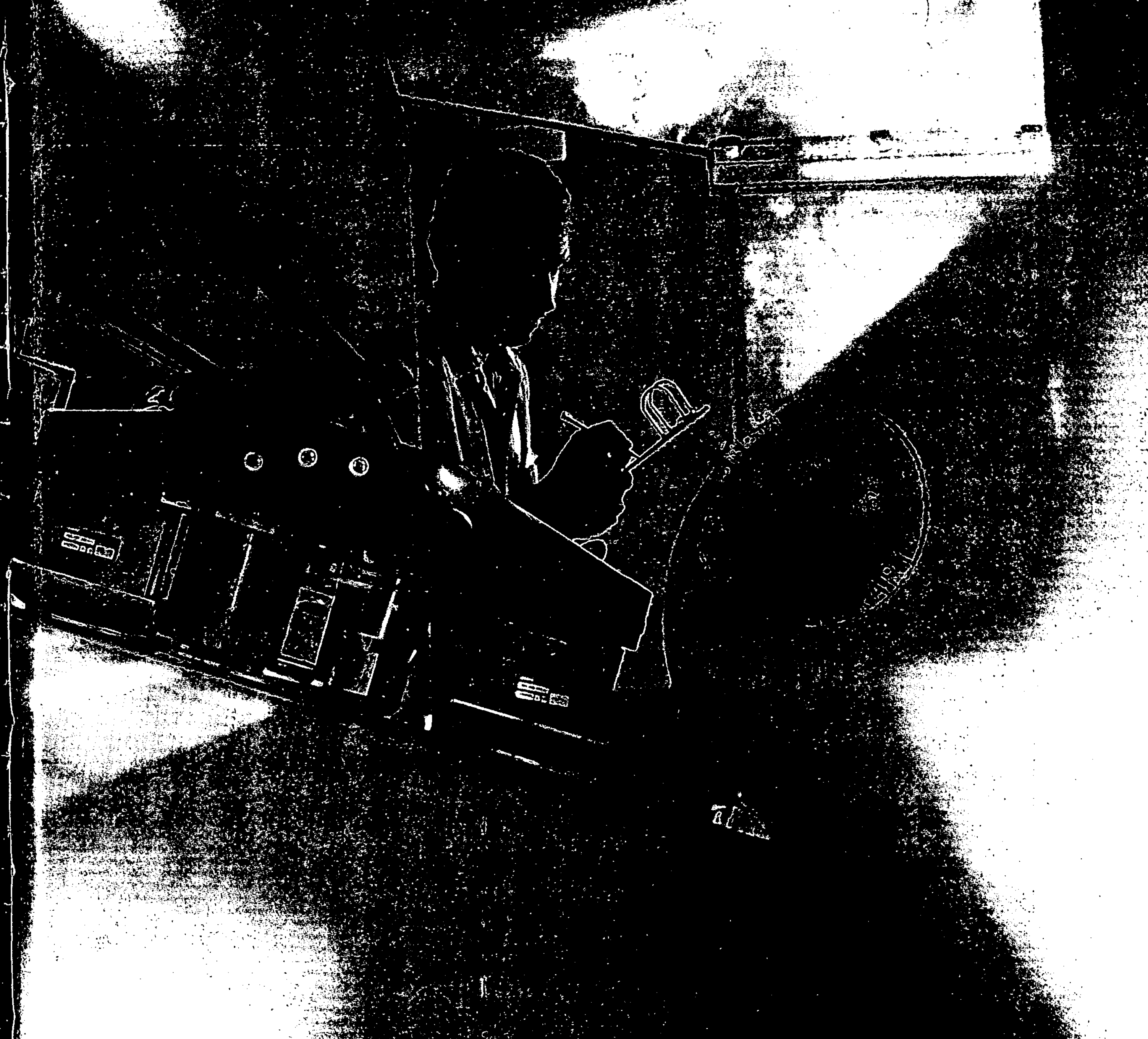
Voith's flotation machine consists of a mixing tank followed by primary and secondary stages with the secondary stage being used to recover useful fibers from the overflow of the primary stage. Each stage is composed of tubular cells arranged in series, the number and size of which depend on the flotation behavior of the printing inks and on the throughput.

According to the supplier, the unit's main advantages lie in maximum brightness with low energy consumption and an above-average purity of deinked stock, due to multiple, consistent, forced ventilation of each cell. Flotation is accelerated because air supply is increased, requiring fewer cells, explains the supplier.

Black Clawson is working with its licensee in Japan, IIM, on the new IIM-BC Flotator flotation cell. According to the supplier, the key to the unit's performance is its ability to mix uniformly high volumes of air into the stock slurry so that maximum brightness and dirt speck removal can be achieved. The air bubbles that are generated by the twin turbines in each cell are evenly distributed across the spectrum of sizes needed to optimize particle-removal efficiency, from 5-500 microns.

Black Clawson claims that the Flotator can improve brightness by 14 points in a single pass, and that it has shown improved speck removal efficiency, even with hard-to-deink grades such as laser-printed office papers or UV-coated grades. The supplier intends to market the Flotator unit on both sides of the Atlantic.

PULP & PAPER
November 1986



CHEMICAL SURVEY:
AMPLE SUPPLIES HOLD PRICES STEADY FOR MOST MAJOR CHEMICALS **45**

COVER STORY:
GEORGIA-PACIFIC STARTS UP NEW UNCOATED FREE-SHEET MACHINE AT PORT HUDSON, LA. **88**

ISSUE FOCUS: CHEMICALS

APPROPRIATE CHEMICAL ADDITIVES ARE KEY TO IMPROVED DEINKING OPERATIONS

Process chemistry should be studied to find the most effective way to deink secondary fiber prior to selecting a chemical additive program

By T.W. WOODWARD

Modern deinking technology has made possible the production of high-quality paper from printed secondary fiber. This technology consists of a careful matching of deinking equipment and chemistry. The performance of deinking systems, whether washing or flotation, is greatly dependent upon the type and concentration of the deinking chemicals.

Another equally important consideration in the selection of deinking chemicals is the fiber furnish. Deinking processing aids are chosen carefully, relative to the type of printed secondary fiber, system type, end product, and percentage of deinked stock in the final product. With proper use of deinking process aids in conjunction with modern deinking facilities, it is possible to achieve brightness and dirt levels equivalent to or better than those of the unprinted secondary fiber.

Given a deinking system type and furnish, there remains a myriad of potential chemical programs suitable for producing the desired grade. Careful laboratory work designed to simulate the system should provide sufficient information to allow trials in the plant, where further changes can be made until optimization is achieved. Knowledge of the function of deinking chemicals will allow blending in order to maximize results.

PRINTING INKS. The classification of printing inks is not rigorous and is based on application, chemical type, drying method, and special properties. These categories are obviously interrelated, with the chemical type being the most important factor when considering the chemistry of ink removal.

Basically, printing inks consist of pigments, providing color and contrast to the ink, incorporated into a vehicle that carries the pigment and binds it to the sheet. Other additives (modifiers) may be used to provide the ink with special properties. Modifiers are usually added in small amounts. The pigment is not soluble in the vehicle and must be mechanically dispersed. With respect to deinking chemistry, it is the vehicle that determines the ease with which inks may be removed from the fibers. Ink vehicles commonly consist of a resin (either natural or synthetic) and a solvent. There are many types of vehicles, their composition depending mainly upon the method by which the ink is dried.

The ink industry is rapidly developing new ink vehicle systems. Unfortunately, the trend appears to be toward vehicles that are increasingly resistant to conventional deinking chemicals. Food & Drug Administration and Environmental Protection Agency regulations tend to inhibit the development of novel chemicals for deinking these chemically resistant inks and varnishes. The thrust in deinking over the last decade has been in development of new technology for mechanical removal of ink particles.

DEINKING PROCESS. Deinking of secondary fiber involves repulping or defibering, during which the ink is removed from the fibers; cleaning and screening; separating ink contaminants from fiber stock; and if necessary, bleaching.

Pulping may be batch or continuous, although the batch method is more commonly used as it provides better control of the process. Some mills prefer continuous pulping as it provides more production for a unit of given size. Chemicals are normally added to the pulper just

Mr. Woodward is a group leader, New Market Research, Betz PaperChem Inc., Jacksonville, Fla. This paper was presented at the chemical procession aids seminar, TAPPI's papermakers conference, New Orleans, La., Apr. 14-16, 1986.

prior to the addition of furnish. Consistencies are usually in the range of 4% to 6%, although there seems to be a trend toward higher-consistency (12% to 15%) defibering with the objective of saving chemicals, heat, and operating manhours.

Where high brightness is necessary, bleaching is required. When high groundwood wastepapers are being deinked, bleaching can be accomplished with peroxides and/or hydrosulfite added to the pulper, although a more efficient utilization of chemicals will be realized if bleaching takes place following screening and washing.[1,2]. Wood-free pulps are usually bleached in a single-stage hypochlorite process, although some mills use an initial chlorination stage followed by hypochlorite. If percentage of groundwood is less than 5%, brightness values of around 80 GE can be achieved.

CHEMISTRY OF DEINKING. The most important determinant of the type and concentration of deinking chemicals is the raw material to be deinked. Next in importance is the design and efficiency of the system. For a given deinking system, changes in furnish type will call for an adjustment in the chemistry of the system. For this article, an efficient cleaning and screening system will be assumed, and the chemistries will be differentiated for low and high groundwood content furnishes.

Removal of ink from paper fibers is accomplished primarily in the pulper and is basically a laundering operation. Water and a large amount of mechanical action are sufficient to remove and disperse most inks, but the level of mechanical energy that is necessary cannot be achieved in a conventional pulper. Chemical energy is thus used in place of some of the mechanical energy.

CAUSTIC SODA. Sodium hydroxide is one of the most important deinking chemicals for woodfree secondary fiber and may be used, with caution, for deinking high groundwood content grades, such as newsprint and coated publication papers. High concentrations of alkali (pH 11.5 to 12.0) can saponify and/or hydrolyze some ink vehicles and will swell fibers to aid in breaking up inks and coatings. The alkali also helps prevent the aggregation of small ink particles into larger ones that are difficult to wash out. The inks on woodfree ledger, computer printout, book, and lightly printed board grades may be effectively removed and dispersed (with the use of other chemicals) at pH values in the range of 10 to 11. Heavily printed and/or varnish-overcoated grades may require a pH of 11.5 or higher.

It is unfortunate that dosages of caustic soda are expressed as a percentage of oven-dried fiber. It is the amount of hydroxide ion that is critical for deinking performance, and the dosage required to achieve a given pH will vary. Sufficient caustic soda should be added to each batch to attain the desired pH. The efficiency of many deinking plants could be increased substantially by better control of sodium hydroxide.

SODA ASH, SILICATES. Sodium carbonate is sometimes used in conjunction with sodium hydroxide. It is said to cook less harshly and produce slightly brighter pulp than caustic soda alone. It is uncommon for soda

TABLE 1: **Deinking processing aids.**

Deinking chemical	Structure formula	Function	Furnish type	Dosage (% of fiber)
Sodium hydroxide	$NaOH$	Fiber swelling-ink breakup, saponification, ink dispersion	Wood-free grades	3.0-5.0%
Sodium silicates	Na_2Si0_3 (hydrated)	Wetting, peptization, ink dispersion, alkalinity and buffering, peroxide stabilization	Groundwood grades Lightly inked ledger	2.0-6.0
Sodium carbonate	Na_2CO_3	Alkalinity, buffering, water softening	Groundwood grades Lightly inked ledger	2.0-5.0
Sodium or potassium phosphates	$(NaPO_3)_n$, n = 15 Hexametaphosphate $Na_5P_3O_{10}$ Tripolyphosphate Tetrasodium pyrophosphate	Metal ion sequestrant Ink dispersion Alkalinity Buffering Detergency, peptization	All grades	0.2-1.0
Nonionic surfactants	$CH_3(CH_2)_nCH_2$-$O(CH_2CH_2O)_xH$ Ethoxylated linear alcohol Ethoxylated alkyl phenols	Ink removal, ink dispersion Wetting, emulsification Solubilizing	All grades	0.2-2.0
Solvents	C_1-C_{14} aliphatic saturated hydrocarbons	Ink softening, solvation	Wood-free grades	0.5-2.0
Hydrophilic polymers	$CH_2CHC{=}OOH(Na)_n$ Polyacrylate	Ink dispersion Antiredeposition	All grades	0.1-0.5
Fatty acid	$CH_3(CH_2)_{16}COOH$ Stearic acid	Ink flotation aid	All grades	0.5-3.0

ash to be used alone due to slower cooking time, but it does provide required alkalinity and buffers at a slightly higher pH than sodium silicate.

Silicates have been used since the turn of the century for deinking wastepaper. Compared with soda ash or caustic alone, silicates provide better ink removal and brighter pulps with less fiber damage.[3] Silicates are complex solutions of polymeric silicate anions. These surface active (detergent) anions are responsible for many of the silicate's deinking functions, such as emulsification and suspension of dispersed ink. This allows deinking to occur at a lower pH, which is effective in high groundwood furnishes, tending to cause less yellowing of the pulp. Silicates seem to work better with small amounts of nonionic surfactants to aid in wetting. The sodium metasilicates are most commonly used. Sodium silicate is a good stabilizing agent in hydrogen peroxide bleaching. Peroxides tend to decompose when they are in the presence of various metal ions. Silicates apparently deactivate these metal ion catalysts and thus control peroxide decomposition.

POLYPHOSPHATES, SURFACTANTS, SOLVENTS. Sodium tripolyphosphate ($Na_5P_3O_{10}$) and sodium pyrophosphate ($Na_4P_2O_7$) are very effective at low concentrations in sequestering calcium and magnesium ions and forming uncolored complexes with cations such as iron.[4] These polyphosphates are also fairly good buffering agents and ink dispersants, and they have detergent properties.

Nonionic surfactants contain an organic part that has an affinity for oils (hydrophobe) and another part that has an affinity for the water phase (hydrophile). The hydrophobic group is usually a long-chained hydrocarbon residue, while the hydrophilic group is an ionic or highly polar group. These surfactants function in deinking systems by lowering the surface tension of water to enable it to "wet" more effectively, absorbing onto surfaces to aid in ink removal and dispersion, and by solubilization and emulsification.[5]

Two of the most common nonionic surfactants used for deinking are the ethoxylated alkyl phenols and ethoxylated linear alcohols. The hydrophilic portion of these surfactants is formed by a polyoxylethylene chain with the degree of hydrophilicity controlled by the number of ethylene oxide units. There appears to be little difference in deinking performance between the two groups of surfactants, although there is evidence that the ethoxylated alcohols perform slightly better on newsprint.[6] Optimum brightness of deinked ledger occurs with nine ethylene oxide units.[7]

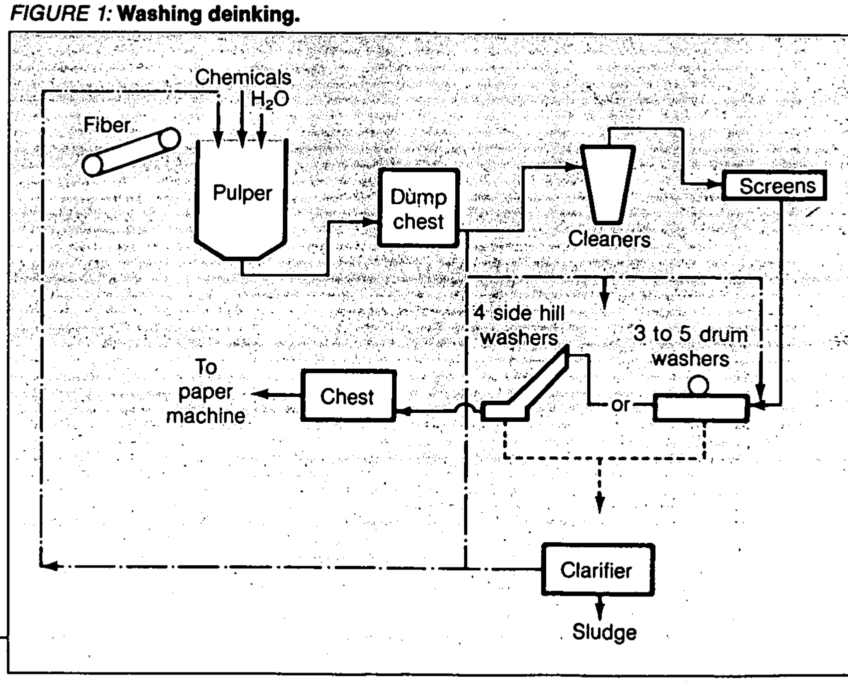
Solvents are available for dissolving most inks and varnishes. Unfortunately, the cost of the majority of these prohibits their use in most deinking programs. Also, in order to function properly in the pulper, a solvent must be insoluble in water at rather low concentrations (less than 1,000 ppm). Many good ink solvents are soluble in water at this concentration and, therefore, solvent-water emulsions cannot be formed. This decreases the solvating power of the solvent. Environmental concerns also limit the use of many effective solvents, such as the chlorinated hydrocarbons. These factors have resulted in aliphatic hydrocarbons being the most common solvents used in deinking systems. Aromatic hydrocarbons are better solvents for most inks, but their higher water solubility negates their greater solvent action. Their use is also limited due to environmental concerns. A surfactant with good oil in water emulsifying properties should be included when using a solvent to ensure good emulsification of the solvent in the pulper.

Although many binders used in inks and varnishes are not soluble in the solvents that are practical for deinking, many of these binders are softened in the presence of a solvent. This allows easier breakup and dispersion by the mechanical action of the pulper and surfactants and dispersing agents that are added with the solvent.

POLYMERS, SOAPS. Hydrophilic polymers are not widely used in deinking programs. Proponents of hydrophilic polymers claim they assist other deinking chemicals in performing detergent functions. Hydrophilic polymers are water soluble, multifunctional organic polyelectrolytes that aid in the dispersion of ink particles and build up electrostatic cleaning forces between ink particles and fiber surfaces. They function similarly to antiredeposition aids in laundry formulation.

Laboratory studies should be performed prior to mill

FIGURE 1: **Washing deinking.**



use of these costly materials. Optimum dosage depends on the chemical environment of the deinking system, and overdosing can have a negative effect on ink removal and dispersion. Two common types of hydrophilic polymers are polyacrylates and carboxymethylcellulose.

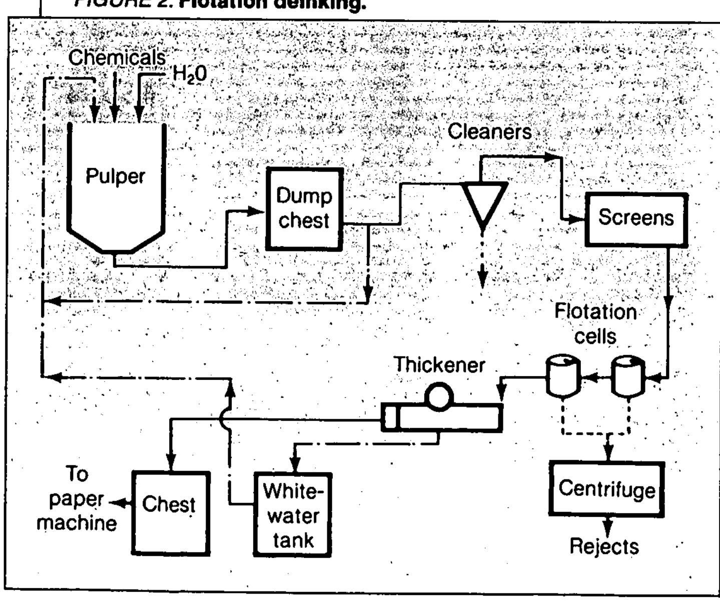
Fatty acid soaps function as collector chemicals in flotation deinking systems. Calcium soaps formed from these fatty acids and calcium ions are the most widely used flotation collectors. Flotation collector chemicals destabilize the ink dispersion and extract the ink particles from the ink-fiber suspension. These destabilized ink particles are attracted to air bubbles in the flotation cell and carried to the surface for removal. Calcium chloride is often added to provide sufficient calcium ion to convert all the fatty acid to insoluble soap.

Newer, more effective flotation collector chemicals (modified polyester resins) have been developed. They are more expensive but are effective at much lower dosage levels. They tend to act as foaming collectors, give more rapid flotation, and do not require hardness ions. The usual dosage is 0.1% to 0.3%.

WASHING AND FLOTATION CHEMISTRY. There are some significant differences in the chemistry of washing and flotation systems. In the washing system, attempts are made to reduce ink particle size to less than 5 microns and to emulsify, dissolve, and disperse as much ink as possible. This results in optimum washing. In flotation systems, reduction of particle size to this level and emulsification of ink are undesirable, as they lead to poor separation in the cells. In combined washing and flotation systems, dispersants should not be added to the pulper but added before washing to aid in the removal of very finely dispersed ink not removed by flotation.

In the flotation system, it is also essential that all collector chemical (fatty acid or soap) be converted to insoluble calcium soap and that all of this chemical is removed by flotation in secondary cells to avoid concentration buildups in process water that would lead to lower efficiencies and machine performance problems.

FIGURE 2: **Flotation deinking.**



EVALUATION OF DEINKING PERFORMANCE. Handsheet or pulp pad brightness and an estimate of dirt or specks are the methods most commonly used in evaluating deinking performance. Other sheet properties that may be important are color and ash content.

For proper evaluation of deinking performance, the objectives of the deinking program must be well specified. It is important that the test methods used in the evaluation adequately reflect the performance of the deinking operation. Brightness and dirt measurements are relatively easy to make, but both require making handsheets or pulp pads. Handsheet making is, in effect, a high dilution washing stage. The loss of fines and ink during sheet preparation may obliterate any quantitative analysis of the particular step being evaluated. Cruea recommends making pulp after dilution to 1% consistency or vacuum draining the pulp—at testing consistency without further dilution—on a 60-mesh screen.[8] These procedures provide close approximations of the condition of the pulp at a particular stage in the deinking operation. TAPPI Standard T213 os-77 ("dirt in pulp") is an adequate method for quantifying ink specks remaining in the pulp. The size (area) of a dirt speck on a sample is determined by comparing it with standard reference specks on TAPPI's dirt estimation chart. Dirt is reported as square millimeters of equivalent black area per square meter of surface examined (ppm).

Another method is to count the number of specks (ink particles) on both sides of the sample and divide by the weight of the sample. Results are reported as specks per gram of fiber. A measure of both TAPPI dirt and specks per gram may be used as a measure of degree of ink dispersion.

The dispersion in a laboratory pulper may be measured by adding small pieces (1 × 0.5 in.) of polyethylene to the pulp shortly before the end of the cook.[9] A clean and ink-free plastic sheet will indicate good ink dispersion, while an ink-coated plastic sheet will indicate poor ink dispersion.

RESIDUAL CHEMICAL EFFECTS. Deinking chemicals have a number of potential negative effects, both within the deinking plant and as a result of carryover into the paper machine.

Foaming may be a problem when surfactants are used as deinking aids. In general, the most effective surfactants for deinking also have the greatest tendency to foam. Proper blending of surfactants will minimize the foam problem while maintaining deinking efficiency. In most systems, this type of foam may be controlled with small amounts of defoamer, and many mills currently using defoamer exhibit no foam problem. Defoamer should not be added to the pulper along with deinking chemicals.

These same surfactants, if carried over to the paper machine, could have a negative effect on sizing, which may cause problems with increased starch and/or coat-

ing penetration. This problem may be alleviated by isolation of the system or by adding size or increasing the level of size addition.

Calcium ion—entering the system as water hardness, as a flotation aid, or in the secondary fiber—may cause deposition on side hill screens and auxiliary equipment. Treatment for calcium carbonate deposition involves the addition of a suitable precipitation inhibitor.

Excess hydrosulfite from groundwood bleaching may hydrolyze to form thiosulfates. Thiosulfates may cause severe corrosion problems. Careful control of hydrosulfite levels or replacement of some hydrosulfite with peroxide should reduce the severity of the problem.

Dispersants and flocculants must be chosen to minimize negative interactions. Dispersant carryover to the clarifiers may reduce their performance, and carryover to the paper machine may cause problems in retention and drainage. Likewise, flocculants in whitewater from the clarifiers could interfere with ink dispersion if carried over to the deinking pulper.

Careful control of flotation collector chemistry is critical; 30% to 60% of the fatty acids added will remain in the pulp and may cause deposition problems downstream. Addition of calcium chloride to provide sufficient calcium ion for formation of the insoluble soap must be carefully controlled. Excess calcium ion may lead to carbonate scaling or be carried downstream to form insoluble calcium soaps with resin acids in pulp. Excess chloride ion may increase corrosion, especially if there is also chloride carryover from bleaching. ■

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CHEMISTRY OF FLOTATION AND WASHING FOR DEINKING NEWSPRINT

INTRODUCTION TO DEINK PROCESS CHEMISTRY

Don McCormick
Process Engineer
Pulp and Paper
Portland, Oregon

ABSTRACT

This paper, the first of a series, will review the topic of recycling, giving a general overview, and will then focus on newsprint deinking. The function of individual chemicals will be discussed, along with ink vehicles, properties of ink, and how to remove ink from the surface of newsprint fibers. Modern deink chemistry is designed to optimize the removal of the vehicle, rather than the pigment alone.

Electrical particle interactions and water affinity are important in deinking and will be discussed. These concepts will form a foundation for understanding the chemistry of flotation and washing presented in the remaining papers.

KEY WORDS

DTPA, deinking, dispersants, displectors, fatty acid soap, flotation, hydrogen peroxide, ink, sodium silicate, and washing.

INTRODUCTION

What chemically happens inside flotation, pulpers, and washing has been a neglected subject area. Many articles have addressed isolated aspects, but none have been published that pull the whole subject together, filling in the missing pieces. This issue cannot be ignored because each recycle plant is designed based on some kind of chemistry model. The more accurate the model, the better the design. Eventually, research in the industry will either confirm or revise the model. In this series, an attempt has been made to pull together pieces from existing mill operations, discussions with experts of both chemical and equipment suppliers, and available articles on deinking to complete a working model of deinking chemistry.

COMMON TYPES OF RECYCLE

Recycle Process	Furnish Grade
Secondary fiber	Corrugated medium Linerboard
News deinking	Newsprint Coated magazines
Ledger deinking	Fine paper
Not recycled	Tissue and towel

WHY ALL THE CONFUSION?

Deinking chemistry has significantly changed in recent years (refer to Tables 1 and 2). The development of process equipment such as high consistency batch pulpers, continuous drum pulpers, new dispersers, new screens, and pressurized flotation cells, along with developments in chemistry such as nonionics, flexographic water-based inks, both alkaline and acid water recycle loops, and water systems independent of the paper machine, have changed the way deinking is done in the United States. These changes have generated confusion about deinking chemistry. Adding to the confusion, major differences exist between North American and foreign deinking systems. Refer to Table 3.

For the past 30 years, many European deink systems have used soap/Ca^{++} chemistry with washing (if present) before flotation. Restrictions on water use, tighter environmental regulations, higher filler content, and the acceptance in the past of products with a lower brightness have caused flotation technology to dominate.

Many Japanese deink systems place flotation before final washing to minimize the mechanical size reduction of ink and stickie particles and because of high amounts of plastic ink in their furnish. Such systems benefit most from using nonionic chemistry. Remaining Japanese systems typically use a washing-flotation-washing sequence and also use nonionics.

Washing and pressing have been the predominant means of deinking in North America (pressing being one form of washing). Recently, many mills have installed flotation cells in addition to washing. The most convenient place to put a flotation cell in an existing wash-only system is where the consistency is about right for flotation (for example, just after reverse cleaning). Therefore, most North American mills have put them in this position, resulting in float-wash systems. Refer to Table 4.

Japanese inks are formulated with plastic resins, as opposed to most North American and European inks which are prepared primarily with vegetable oil vehicles. Additional pulping energy and process steps are required to remove plastic ink from the surface of pulp fibers. Some deink mills are installing dual pulper systems: one system for news and another for magazine. They feature <u>continuous</u> gentle drum pulping at high consistency and <u>low pH</u> (8) for news furnish, using only silicate or alkali (sodium carbonate) and nonionics in the pulper; and for magazine furnish, <u>batch</u> pulping at high consistency (15%) and <u>higher pH</u> (10), using a wide range of chemicals in the pulper.

DEINKING CHEMICALS USING SOAP/Ca^{++}

Deink Chemicals

- Alkali - swelling, fibrils, pH, saponification
- Soap - micelles, froth generation, stearate
- Sodium silicate - alkali, buffer, sequesterant, water softener, metal passivator, deposits, emulsifier, reduce friction, not selective
- Hydrogen peroxide - maintain brightness
- Chelant - complex metals, selective, disassociation
- Calcium chloride - hardness, precipitate soap

Alkali (Sodium Hydroxide or Sodium Carbonate)

The presence of alkali in the pulper causes fibers to swell and opens up fibrils. Alkali partially breaks down vegetable oil ink vehicles by saponification and controls chemical species in solution (such as DTPA) by pH (refer to Figure 1). Alkali increases the peroxide bleaching action by pushing the reaction toward the active bleaching agent, perhydroxyl ion.

$$H_2O_2 + OH^- \rightarrow H_2O + OOH^-$$

The perhydroxyl ion reacts with lignin, forming acids that are neutralized by alkali.

Soap

Deink Surfactants
• Soap/Ca^{++} used in news systems primarily in Europe
• Nonionics, also called dispersant/collectors or displectors, used in news systems primarily in North America and Japan
• Mill proprietary surfactant formulations not normally used in news systems (example: Fort Howard tissue)

Soap in a household washing machine or dishwasher encapsulates dirt to form many small colloidal particles called micelles. Fatty acid soap is used for ink dispersion in deinking by micelle formation, providing active sites for ink on flotation bubbles and as a froth generating agent. (Micelles will be further discussed in the next paper.) Soap is added ahead of the flotation cells to form stearates and often at the pulper for ink removal.

Cloud point temperature is usually an important consideration when selecting a surfactant. Below this temperature, the solution is murky (suspended solids) stabilizing foam, and above this temperature it is clear (dissolved solids) and foam generation is reduced. However, unlike traditional surfactants, reacted nonionics both froth and form micelles above and below their cloud point (about 130°F). For nonionics, micelle formation usually increases dramatically as a surfactant's cloud point is approached.

Sodium Silicate

Sodium Silicate's Role
• Source of alkali
• Buffers pH at 11.3
• Sequesters metal ions
- Peroxide stabilizer
- Softens water
- Random, not selective
• Surfactant, detergent
- Emulsifies vegetable oil ink vehicles
• Metal surface passivator
- Coating agent
- Corrosion inhibitor
• Reduces particle friction
- Increases solution viscosity
• Peroxysilicates
• Claimed to be a penetrant
• Forms deposits
• Disturbs water clarification

Sodium silicate is added at the pulper. It is a complex polymer and source of alkali, which acts as a pH buffer at 11.3.

$$Na_2SiO_3 + H_2O \rightarrow Na^+ + OH^- + HSiO_3^-$$

However, its main task is to sequester metal ions. It softens water by flocculating (sequestering) ions like calcium and magnesium that form insoluble deposits with surfactants used for frothing and fiber wetting. True chelants, however, are needed for other metals. Silicates have detergent properties that disperse and emulsify vegetable oil ink vehicles. It is also a metal surface passivator for corrosion. If fed improperly, it may form glassy deposits and may also interfere with water clarification in recycle loops. Silicate reduces particle friction so the particles in suspension can slip past one another more easily. Any carryover of silicate to the paper machine wet end may hurt retention aids.

Hydrogen Peroxide

Hydrogen peroxide, added at the pulper, is used to bleach mechanical pulp yellowed from the action of alkali on lignin, but usually only enough to maintain the original furnish brightness. Not enough peroxide results in yellow pulp where the brightness cannot be completely regained after bleaching. Too much results in hardening ink drying oil vehicles. There are two schools of thought about peroxide. One is that it prevents the formation of colored chromophoric groups in lignin (double bonds near aeromatic rings), the same as it prevents brightness reversion in chemical pulp. The other is that peroxide does <u>not</u> prevent chromphoric groups from forming, but oxidizes them once they have formed to make them colorless. In either case, the pulp is brightened. A negative property of peroxide is that, as an oxidant, it hardens the drying oil vehicles in ink. If peroxide disassociates to oxygen gas and water, the oxygen bubbles, being very tiny, may tend to collect at fiber/ink interfaces, assisting in the removal of the ink particles from the fiber surface. Dissociation is slightly exothermic and strongly auto-catalytic, self-propagating at an increasingly faster rate.

Chelant (DTPA, Polyacrylates, or DTPMPA) - Refer to Figure 2

Metal ions come from wood fibers, mill water, equipment (e.g., refiner plates), ink formulations, and additives (e.g., alum and caustic). Chelants are used to tie up metal ions by forming complexes that prevent the ions from catalyzing the dissociation of

hydrogen peroxide. It permanently surrounds and uses up all of a metal ion's coordination covalent bonding sites. In separation process, as the metal/chelate complex will go with the water fraction.

DTPA will immediately complex with the metal ions it first encounters. Then, as it moves within the solution, it will release ions of lower priority and complex ions of higher priority. This preference makes DTPA selective toward particular ions compared to silicate. This priority, at a pH of 10, is: $Ni^{++}>Cu^{++}>Co^{++}>Fe^{++}>Pb^{++}>Zn^{++}>Mn^{++}>Fe^{+++}>Ca^{++}>Mg^{++}>Al^{+++}$ (refer to Figure 3).

Chelants complex with only ionized or oxidized metals, not metal atoms in the free metallic state. Because DTPA is an amine, it will be slowly oxidized by peroxide and, therefore, should be mixed with the pulp before the peroxide feed point (half will be oxidized within one hour). DTPA is more stable toward peroxide than EDTA, and DTPMPA is reported to be more stable than DTPA.

Calcium Chloride

Calcium chloride is usually added just before flotation. It provides additional water hardness to change hydrophilic (water-loving) ink micelles to hydrophobic (water-hating) and precipitates excess soap in the flotation cell solution onto bubbles to create active sites for easy adsorption of ink particles. These reactions are similar to the formation of scum in a household shower or the graying of clothes from hard water deposits in a household washer. Calcium chloride will also precipitate any excess silicate from the deink pulper. Lime can also be used as a source of calcium ions and will be discussed in the third paper in this series.

Clay

The role of clay in deinking will be discussed in the next paper in this series as part of the section on flotation.

Sulfuric Acid

Diluted sulfuric acid is usually added after bleaching to adjust the deinked stock pH to that of the paper machine white water and to prevent color reversion by alkali. During this neutralization process, many solid precipitates (e.g., $CaSO_4$ when using soap/Ca^{++} and organic salts) are formed that should be removed before sending the pulp on to the paper machine.

For a summary of deink chemical usage, refer to Table 5.

PROPERTIES OF INK

Following are the ingredients in ink:

Pigment
Carbon black

Vehicles
Vegetable drying oils
Mineral oils
Varnish and solvent
Lacquers
Shellacs
Acrylic and other plastic solutions and emulsions
Nitro and other cellulose derivatives

Modifiers
Clays
Waxes
Rosin
Glycol
Gums
Rubber
Defoamers
Silicones

Printing ink is a complex mixture of ingredients, including pigments, vehicles, and modifiers. It also contains transition metals such as lead (Pb) and chrome (Cr) that will dissociate hydrogen peroxide to water and oxygen. The sequence of process steps in a deink plant is partly determined by the chemistry of the ink removed.

Types of Ink Vehicles

- Non-polymeric vegetable oil
- Polymeric drying oil
- Plastic
- Water base

Dispersable ink is a combination of carbon black pigment suspended in a vegetable oil, hydrophobic vehicle. Since the pigment is held tightly by the vehicle, the vehicle must be chemically modified (saponified) so the pigment can be removed.

Deink chemicals are specific for modifying and removing vehicles. The pigment, entrapped with the vehicle, is also removed, but indirectly. If the ink vehicle is changed from oil-based to water-based, the deink flotation process, so far, has not efficiently removed it. Overly aggressive chemicals that free the carbon black from the vehicle should be avoided in flotation (but would help washing) because the deink flotation process removes vehicles rather than free pigment.

There are two types of vegetable oil vehicles: nonpolymeric saturated such as corn, peanut, or coconut and drying oils such as tung, safflower, or linseed that slowly polymerize (cross-link) to a hard surface by exposure to oxygen or oxidants like peroxide. Peroxide in the pulper accelerates the setting of drying oil vehicles.

In waste news, the vehicle can be a vegetable oil paste (offset letter press and rotogravure) or a hard plastic solid (ultraviolet, heat set, Xerox, laser, inkjet). Because paste vehicles are rubbed off a

newspaper onto the reader's hands and they give a less crisp printed image, the trend is toward the use of plastic vehicles..

Typically, four different forms of ink are received in the furnish of a deink plant:

- Paste vegetable oil ink that can be chemically dispersed by saponification reactions with alkali (refer to Figure 4).

- Drying oil, dried, and polymerized vegetable oil ink that can be saponified, but requires more time, higher alkali concentrations, and heat (refer to Figure 5).

- Dried and polymerized vegetable oil ink on coated magazine inserts. In this case, the ink is not attached to paper fibers, but to a clay coating that disintegrates in the pulper by mechanical rubbing. Some coatings are not clay based, but are thin cured plastic films. These are rare in news deinking. They will partially disintegrate in the pulper to small, visible, colored specks or flakes.

- Hard plastic inks that, when printed directly on fibers rather than on a clay coating, are removed only by fiber-to-fiber rubbing and shear (refer to Figure 6).

Hard plastic inks usually contain polymer resin, or varnish and solvent, and are heat- or light-fused after electrostatic attraction or printing onto coated paper. Once fused and hard, these inks become nondispersable. The three types of ink, vegetable oil, drying oil, and plastic, are progressively more difficult to disperse. United States newspapers are starting to use plastic ink for both inserts and the front page. It is expected that this trend will continue.

Several newspaper publishers have recently changed to "water-based" hydrophilic flexographic ink formulations rather than the traditional vegetable oil hydrophobic vehicles. Publishers cite the advantages of no rub-off printing, lighter basis weight sheets, and less show-through. Flexographic ink has not yet been commercially removed by flotation cells. Washing soon after pulping will separate the flexo ink from the pulp fibers. However, the challenge is to clarify this washer filtrate so the water can be reused. This problem is a topic of current research interest.

DYES

A distinction should be made between inks, in which carbon black is used as a pigment, and dyes. A pigment is an insoluble, usually inorganic, colored powder trapped among pulp fibers. Dyes are usually soluble unsaturated aromatic organic molecules attached to fibers. The molecules give color to fibers by adsorbing selected wavelengths of light. Since they are molecular soluble liquids rather than large solid particles, washing and flotation processes do not remove dyes. Basic dyes, used for most wood-containing grades such as news, are chemically broken down by reductive bleaching (hydrosulfite), but most are unaffected by oxidative bleaching (peroxide). Neither domestic bleaching process affects yellow stilbene dyes, and bleaching does not affect pigments. However, reductive FAS is claimed to attack stilbene dyes.

Pigments	Basic Dyes
Insoluble	Soluble
Inorganic	Organic aromatics
Powder	Molecular
Colored	Adsorb light
Trapped	Fixed
Not affected by bleach	Reductive bleaching

STICKIES

Stickies are small tacky accumulations that concern both printer and paper maker by sticking sheets of paper together inside a paper machine reel. Stickies can cause the following problems:

- Stick sheets in a reel together
- Sheet breaks
- Sheet holes
- Paper defects
- Pipeline deposits
- Solvent cleaners
- Poor slitting
- Printing problems
- Deposits on rolls
- Slower machine speed
- Picking
- Deposits on dryer cans
- Press room breaks

Stickies may be trapped in the pores of paper machine felts and wires, causing breaks, holes, and other paper defects. Stickies are made of many different materials, including waxes, glues, hot melts, styrofoam, pulpable plastics, rubber, dried latex, and pressure-sensitive adhesives that are partially modified and degraded by pulping chemicals and processes. Sources include adhesives, ink vehicles, coating binders, and furnish contamination.

The removal of stickies is a complex topic covered well by other papers, but certain key points should be reviewed. Stickies can be removed by size, density, or chemically by their hydrophobic properties. Another approach is to "detackify" them if they are not subjected to high shear that exposes new surfaces. To prevent breaking down the size of stickie particles and dispersing them, gentle low-shear pulping at low temperatures should be used. Coarse screens remove large stickies. Fine screens and reverse cleaners remove medium size, and flotation removes most small stickies. Because they are hydrophobic, many stickies of the same particle size as ink may be floated out at the cells. It is important to remove large stickies whole before high shear operations break them down into small particles. A few large stickies are easier to remove than many small ones.

REMOVING INK FROM THE FIBER SURFACE

Ink must be removed from the surface of pulp fibers and suspended in water so that it can be removed with the filtrate during washing or interact with bubbles during flotation.

Ink particles are removed from the surface of fibers by four actions:

- Swelling of fibers and opening of fibrils by alkali (caustic and silicate)

- Mechanical rubbing action of other fibers and shear from agitators, pumps, etc.

- Heating to produce more vigorous chemical action (faster kinetics and increased solubility) and mechanical action (reduced viscosity).

- Chemical solvation by water due to micelle formation.

The first three are the primary methods for removing hard plastic inks. Micelles are formed with hard plastic ink vehicles only after they have been removed from the fiber surface by mechanical methods. Surfactants cannot penetrate the surface in the same manner as with vegetable oil vehicles. No saponification or solvation is involved. After moderate mechanical action, hard plastic ink tends to form long, thin, cylindrical particles rather than the spherical particles of oil ink vehicles. When the presence of these particles is visible in a finished sheet, they appear as black hairs.

WHY IS HYDROPHILIC/HYDROPHOBIC IMPORTANT?

Particles in deinking solutions interact in two ways: surface charge attraction and repulsion, and affinity for water.

Hydrophobic molecules are water-hating, three dimensionally symmetrical, oil-like molecules that are electrically neutral. Hydrophilic molecules are water-loving and geometrically unsymmetrical, causing a negative and positive end to the molecule. This is important because like compounds will mix with each other: hydrophilic compounds such as water will mix with other hydrophilic compounds such as alcohol; hydrophobic compounds (e.g., oil) will mix with other hydrophobic compounds (e.g., fats). Hydrophilic compounds will not mix with hydrophobic compounds. This concept of the affinity particles have for water will be the basis for the next paper in this series.

SUMMARY

The major chemicals in news deinking have been introduced, with how they entered the system and their relevant individual properties. The next paper will explain how these chemicals interact in a wash-float system to remove ink and stickies and will extend that explanation to float-wash systems.

REFERENCES

Sources will be given in the last article in this series.

TABLE 1

SHIFTS IN DEINKING CHEMISTRY

Soap/Ca^{++}	→	Nonionic surfactants
Reductive bleaching (except FAS)	→	Oxidative bleaching
Single-stage bleaching	→	Multistage
Oil-based inks	→	Water-based flexographic inks and plastic inks
Combined water systems	→	Separate
Alkaline deinking	→	Combined alkaline and acid

TABLE 2

SHIFTS IN DEINKING EQUIPMENT

Low consistency pulpers	→	High consistency
Tub pulpers	→	Drum pulpers
Pulper trash removal by rope	→	Whole
Deflaking	→	Disperson
Refining dispersion	→	Fiber rubbing disperson
Atmospheric float cells	→	Pressurized flotation
Flotation or washing only	→	Both flotation and washing

TABLE 3

FOREIGN VS. NORTH AMERICAN DEINK SYSTEMS

Location	Deink System	Chemistry	History
Europe	float only	soap/$CaCl_2$	traditional
	wash-float	soap/$CaCl_2$	modern
	float-wash-float	soap/$CaCl_2$	modern
	Reasons: lower water use, tight environment, lower brightness accepted in the past, and high filler content		
Japan	float-wash	nonionic	traditional
	wash-float-wash	nonionic	modern
	Reasons: plastic ink, prevent size reduction of ink and stickies, and lower brightness accepted		
North America	wash only	nonionic	traditional
	float-wash	nonionic	modern
	Reasons: high brightness, vegetable oil based ink, and prevent size reduction of ink and stickies		

TABLE 4

NORTH AMERICAN NEWS DEINK SYSTEMS

Mill A	wash only
Mill B	wash only
Mill C	wash only
Mill D	wash only
Mill E [1]	wash-float
Mill F	wash only
Mill G [2]	wash-float-wash (old line)
Mill G	float-wash (new line)
Mill H	float-wash
Mill I	float-wash
Mill J	float-wash
Mill K	float-wash
Mill L	float-wash
Mill M	float-wash
Mill N	float-wash
Mill O	float-wash
Mill P	float-wash
Mill Q	float-wash

[1] Remove ink from froth flotation clarifier on washer filtrate; system is primarily flotation.

[2] Only one float cell in a train of washers; system is primarily wash-only.

Mill names are withheld to protect privacy.

TABLE 5

DEINK CHEMICAL USAGE

Sodium hydroxide	NaOH	1-2%
Soap or fatty acid	--	0.5-0.8%
Sodium silicate	Na_2SiO_4	2-4%
Hydrogen peroxide	H_2O_2	1-3%
Chelant	DTPA	0.1-0.3%
Calcium chloride	$CaCl_2$	0.2-0.6% (200 ppm hardness)
Dispersing agent	--	0.1-0.4%
Clay	Alumino silicate	1-7%
Sulfuric acid	H_2SO_4	0.1-0.4%
Polymers (for clarification and sludge)	--	0.5-2%

FIGURE 1

Distribution of chemical species in DTPA solution vs pH

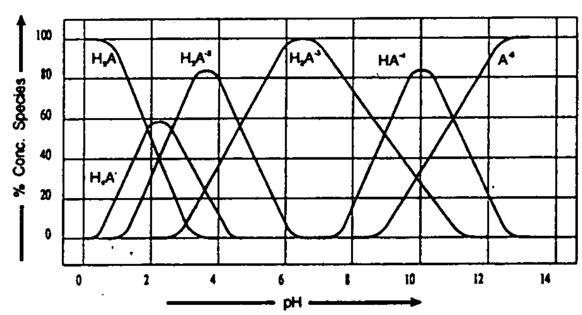
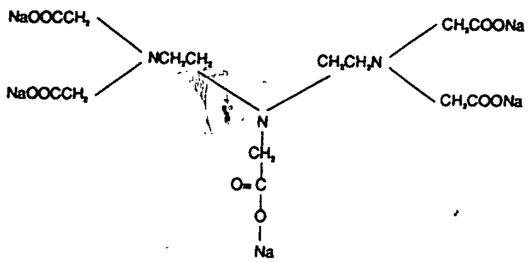


FIGURE 2

DTPA Diethylenetriaminepentaacetate sodium salt



DTPMPA Diethylenetriaminepentamethylene phosphoric acid

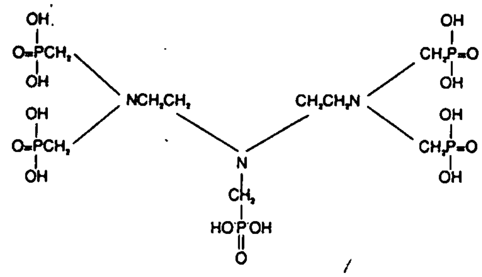
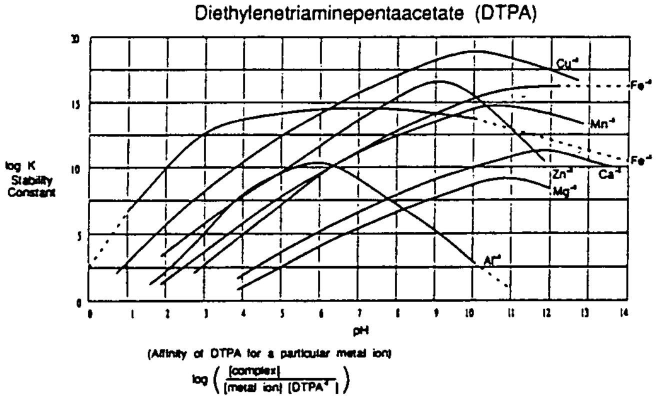


FIGURE 3

Diethylenetriaminepentaacetate (DTPA)



$\log\left(\frac{[\text{complex}]}{[\text{metal ion}]\,[\text{DTPA}^{5-}]}\right)$

FIGURE 4

Nonpolymeric vegetable oil ink vehicle on uncoated paper

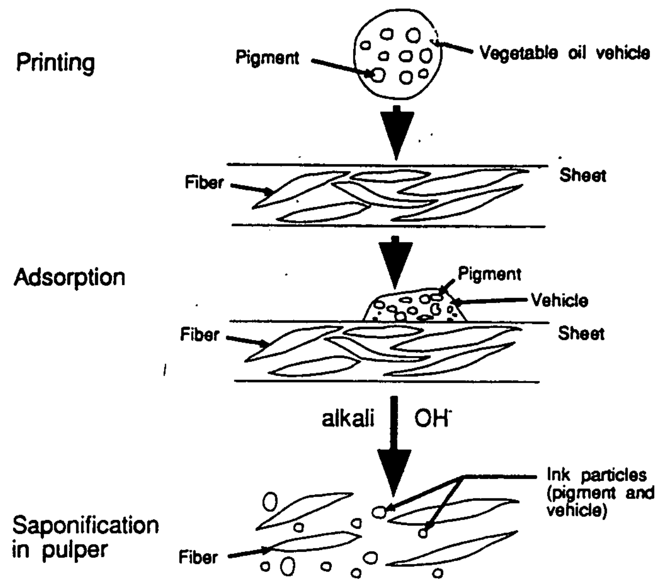


FIGURE 5

Polymeric drying type vegetable oil ink vehicle on uncoated paper

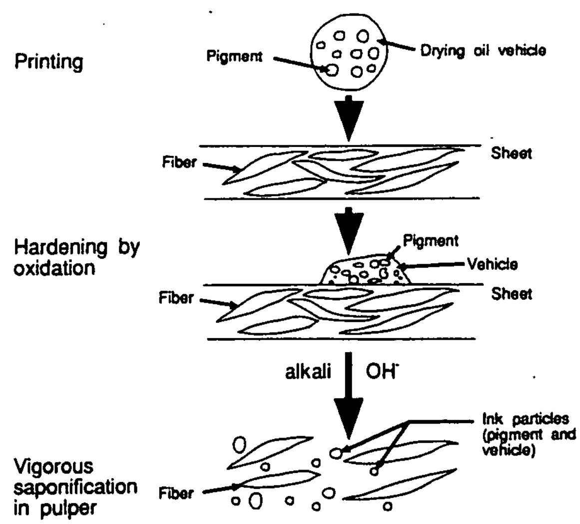
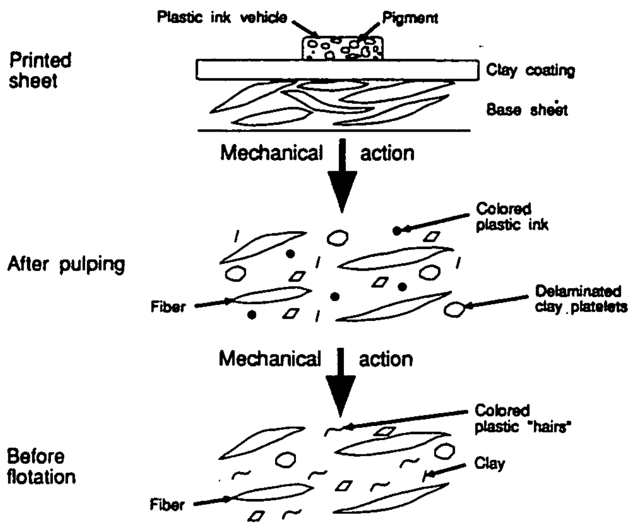


FIGURE 6

Plastic ink vehicle on coated paper



DECLARATION OF DOUGLAS E. EVELEIGH, PH.D.

Patents

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:	)	
Ow et al.	)	
Serial No.: **09/121,152**	)	Art Unit: **1731**
Filed: **May 6, 1994**	)	Examiner: **Steve Alvo**
For: **BIOLOGICAL DE-INKING METHOD**	)	

DECLARATION OF DOUGLAS E. EVELEIGH, PH.D. UNDER 37 CFR § 1.132

DOUGLAS E. EVELEIGH, PH.D., declares as follows:

1. I earned a Ph. D. in mycology in 1959. Subsequently, I have conducted extensive research in the fields of enzymology, microbiology and biochemistry at Rutgers, the State University of New Jersey. I was recently awarded the Chair in Applied Microbiology, the Eveleigh-Fenton Chair. My studies for 30 years have addressed the roles of bacteria and fungi in wood degradation, including application of the activities of microbes to the good use of mankind. Applications are diverse, ranging from gasohol production from wood through conversion of cellulosics to alcohol by action of cellulase enzymes and alcohol producing bacteria such as *Zymomonas* species, through to novel deflatulence enzymes (Beano type) stable at boiling cooking temperature. Attached is a copy of my Curriculum Vitae.

2. My declaration is based on my scientific experience and understanding of the subject matter as an expert in the art. I am familiar with the invention described in the above-identified patent application regarding the novel use of deinking enzymes under non-alkaline conditions.

3. I have read the English translation of Japanese Patent 59-9299 ('299 patent). In my expert opinion, the '299 patent, read in its entirety, teaches

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one of ordinary skill in the art only the successful use of deinking enzymes with alkaline deinking chemicals. It is my opinion that the data provided in the '299 patent, taken together with the knowledge of one skilled in the art prior to the priority date of the present application of May 16, 1989, does not provide an expectation for the successful use of enzymes for removing ink from pulp in a non-alkali environment, in particular at a pH of between about 3 to about 8.

4. This is true because the overall thrust of the '299 patent specification, and the evidence provided in all preferred embodiments and in all the Examples, refer to only alkaline deinking conditions. The statement on page 2, last full paragraph, to page 3, end of carryover paragraph, that

> [a]ccordingly, this invention provides a de-inking agent for recycling old paper, containing cellulase. Cellulase commonly occurring in plants, animals, bacteria and fungi can be used in this invention without any special restriction, but alkaline cellulase is especially preferred. Alkaline cellulase is one having optimum pH 8.0 – 11.5 (preferably 8.1 - 11.0). Such enzyme retains its activity in the alkaline range as well as the acid or neutral range, e.g. a product purified and fractionated from cellulase culture liquid of various origins by salting out, precipitation, dialysis and gel fractionation . . .

refers to the conditions under which the enzyme may be purified, and does not suggest the use of the enzyme for deinking under non-alkaline conditions. Even if one were to interpret the statement to indicate the use of the enzyme under non-alkaline conditions, one skilled in the art would not have expected a successful result deinking under non-alkaline conditions, for the reasons described below. The only scientifically supported statements in the '299 patent are directed to the use of deinking enzymes in alkali conditions.

5. A possible reading of the '299 patent is that it is possible for cellulase enzymes to have activity at all pH ranges, but one skilled in the art at the time of this invention would not have tried to deink at a neutral pH, or non-alkaline conditions, because it was thought that alkaline conditions were required to achieve the swelling of the fibers necessary to remove the ink particles.

6. Before the description in the above-identified patent application, it was believed that alkaline conditions were necessary to cause ink containing paper fibers to swell to effect defiberization and deinking by enzymes. Absent alkaline conditions, one would not have expected swelling, and therefore deinking, to occur as a result of the addition of deinking

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enzymes alone in the pulping process. In the deinking art there is over twenty years of published detailed studies from commercial, academic and government laboratories that emphasize that chemical modification and treatment by alkali exposure is essential and necessary for deinking. As a recent example, enclosed is a copy of the Paper and Pulp International (PPI) publication entitled "Neutral Deinking Makes Its Debut," describing the breakthrough in October 1993 of deinking in neutral conditions, without the addition of alkalis such as sodium hydroxide to the pulp prior to or during deinking.

7. Therefore, to one skilled in the deinking art at the time the above-identified application was originally filed, the deinking action of enzymes in a non-alkaline medium would have been both novel and surprising. An expectation of the successful use of deinking enzymes in an aqueous medium having a pH of between about 3 to about 8 is not found in the '299 patent. It is my opinion that prior to the invention described in the above-identified patent application, no one skilled in the art would have considered evaluating deinking enzymes alone without the addition of alkalis.

8. In summary, it is my expert opinion that the disclosure of the '299 patent supports only the deinking of waste papers by the use of chemical alkaline deinking agents and cellulase, and does not provide a basis for the successful use of cellulase deinking enzyme in an aqueous medium having a pH of between about 3 to about 8 with an expectation of successful deinking of waste paper.

9. The undersigned declares that all statements made herein of his own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements are made with the knowledge that willful false statements and the like are punishable by fine or imprisonment or both under 18 U.S.C. § 1001, and that such willful false statements may jeopardize the validity of the above-referenced application or any patent issuing thereon.

April 12 2004
DATE

DOUGLAS E. EVELEIGH, PH.D.